

## A new view on sulfur speciation in geological fluids at elevated temperatures and pressures

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The amount and chemical speciation of sulfur in geological fluids are controlling factors in the formation of magmatic-hydrothermal deposits of many economically critical metals [1]. The two major forms of sulfur in crustal fluids over a wide range of temperature and pressure are believed to be sulfate ( $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ ) and sulfide ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$  and  $\text{S}^{2-}$ ). They are regarded as the key agents controlling the transport and precipitation of metals by deep and hot fluids. However, this belief is based almost exclusively on observations of sulfate and sulfide in minerals, silicate glasses, and fluid inclusions brought to the Earth's surface and/or extrapolations of thermodynamic data for most aqueous sulfur species obtained at near-ambient conditions. It thus suffers from the lack of *in situ* approaches for analyzing sulfur in geological fluids and melts at elevated temperatures and pressures.

In this keynote contribution, we present *in situ* measurements using Raman spectroscopy [2] in model sulfur and thiosulfate aqueous solutions and vapors across a wide range of acidity (pH~2–8), sulfur concentration (0.3–6 wt%), temperature (150–500°C), and pressure (5–50000 bars). Results show that sulfur in the low-density vapor phase is represented by  $\text{H}_2\text{S}\pm\text{SO}_2$ . In contrast, the dominant stable sulfur species is the dense liquid and supercritical fluid phase is the trisulfur ion  $\text{S}_3^-$  that forms rapidly and reversibly at the expense of sulfide and sulfate above ~250°C in a wide pressure and acidity range. The large stability of  $\text{S}_3^-$  may favor the mobility of sulfur and chalcophile metals such as Au, Cu and Pt in hydrothermal fluids over a range of depth, and thus provide the source of these elements for the important types of gold deposits in Achaean greenstone belts and porphyry-epithermal systems.

[1] Pokrovski *et al.* (2008) *Earth Planet. Sci. Lett.* **266**, 345–362. [2] Pokrovski & Dubrovinsky (2011) *Science* **331**, 1052–1054.

## Structural study of copper chemical status adsorbed onto and incorporated by benthic algae and periphytic biofilm

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While the major macroscopic parameters of metals interactions with inorganic constituents of continental aquatic systems are well known, the role of biota remains poorly understood. Here we studied the interaction of one of the most phyto-toxic metals, copper, with different phototrophic microorganisms as a function of exposure time via physico-chemical characterization of metal adsorption on and incorporation into cells under controlled laboratory conditions. For this purpose, we have combined two different approaches, the 'macroscopic' stable-isotope techniques with the 'microscopic' molecular-level observations using XAS spectroscopy of the complexes formed.

Results show that drastic changes in local chemical environment of copper occur upon its adsorption onto or incorporation in the cells, similarly to Zn and Cd [1-3]. To investigate the local atomic environment of Cu in periphytic biofilms, freeze-dried samples with 1 to 5000 ppm Cu were examined by XAS at ID26 beamline (ESRF). The high-resolution mode, for the first time used for copper in biological matrices, allowed establishing specific features of the Cu pre-edge and quantifying the oxidation state and nature and number of neighbours around Cu. Low-concentrated samples (1-20 ppm), demonstrate the presence of sulfur in the nearest atomic shell of Cu, whereas in concentrated samples, carboxylic complexes of Cu predominate. These findings help establish the interaction mechanism of autotrophic photosynthetic microorganisms with copper at trace and toxic level. The results of this integrated study can be useful for tracing the environmental effects of metal-biota interactions, and may provide new insights on the mechanisms of Cu stable isotope fractionation in biological systems.

[1] Guiné *et al.* (2006) *Environ. Sci. Technol.* **40**, 1806–1813. [2] Pokrovsky *et al.* (2005) *Environ. Sci. Technol.* **39**, 4490–4498. [3] Pokrovsky *et al.* (2008) *Geochim. Cosmochim. Acta.* **72**, 1742–1757.